Effect of Interfacial Strengthening in Blends of Reclaimed Rubber and Polypropylene

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ABSTRACT: Thermoplastic vulcanizates (TPVs) were prepared from polypropylene (PP) and reclaimed ground tire rubber crumbs. Three types of interfacial strengthening agents—degraded PP, hydrosilylated PP, and hydrosilylated PP grafted onto styrene-butadiene rubber—were prepared in melt via a stepwise series of reactions and employed to generate various degrees of interfacial adhesion in the aforementioned blends. The incorporation of the interfacial agents resulted in improvements in the mechanical properties of these TPVs, and the rubber particle size remained constant. The PP chain length and the functional groups present in the interfacial agents affected the magnitude of the improvement in the mechanical properties. The interfacial agents were primarily present on the surface of the rubber particles in the

INTRODUCTION

Continuous efforts in our community to recycle crosslinked rubber products have led to the successful launch of commercially available rubber crumbs in the market.¹⁻⁵ The reclaimed rubber crumbs are obtained by the mechanical shredding and grinding of used rubber products into particles of various sizes, which are still thermosets. Their compounds with thermoplastic binders have low mechanical strength because of the poor adhesion between the rubber particles and the polymer matrix. Debonding and crack formation at the interface of these materials occur under stress as the sharp edges along the irregular shapes of the rubber particles are centers of stress concentration.^{6–12} Thus, rubber crumbs have found only limited uses in low-performance applications for which the inferior mechanical properties are not crucial.

Crosslinked rubber particles are formed in thermoplastic vulcanizates (TPVs)^{13,14} during dynamic vulblends, as shown by energy-dispersive X-ray spectra. These interfacial agents in the PP/rubber crumb blends led to a unique preyield kink in their stress–strain curves, a plateau, or a sharp turning point in the region of approximately 3% elongation and approximately 4-MPa stress. These kinks were interpreted similarly to the cold flow of semicrystalline polymers in tension. The addition of the interfacial modifiers decreased the shear viscosity and increased the entrance pressure drop in flow through capillary dies, and this was attributed to changes in the elongational viscosity of the blends. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1051–1059, 2010

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canization of virgin rubbers and thermoplastics. Excellent adhesion to their embedded thermoplastic matrix allows the rubber particles to absorb the mechanical energy applied, and this provides high resistances to mechanical tearing, stretching, and compression. The interfacial adhesion in these materials is due to the high compatibility between the rubber phase and the thermoplastic phase, which is achieved sometimes by small amounts of compatibilizers that are added or created in situ. Fine dispersions or interpenetrating phase structures are developed on a micrometer scale, and they result in superior mechanical properties.⁶ These conventional TPVs set the upper limit of improving the interfacial adhesion between crosslinked particles and thermoplastic matrices for compounds made from recycled rubber crumbs and thermoplastics. It is thought that the size of recycled rubber particles cannot be changed by compatibilization techniques, but coupling by interfacial agents/copolymers would be helpful in strengthening the interface. Enhanced properties resulting from such interface strengthening can make the compounds competitive in value-added applications because of the cost and processability.

Particle size and interfacial adhesion^{12–14} are two important factors affecting the mechanical properties of TPVs. Various compatibilization techniques are very effective in enhancing the mechanical strength

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Material	Description	Supplier/manufacturer		
PP	HY6100 (melt flow index = 1.2 g/10 min)	Basell		
RC80	80 mesh (180 μm)	SOTA Environmental Research Group		
SBR	Virgin rubber			
PDMS	Hydride-terminated polydimethylsiloxane (DMS-H03)	Gelest, Inc.		
Pt catalyst	Platinum divinyltetramethyldisiloxane complex	Gelest, Inc.		
Cocatalyst	Anhydrous <i>t</i> -butyl hydroperoxide in 5–6 <i>M</i> decane	Gelest, Inc.		
Organic peroxide	Luperox 101 [2,5-bis(<i>t</i> -butylperoxy)- 2,5-methylhexane]	Atofina Chemicals		
S	Crosslinker	Aldrich-Sigma, Inc.		
TMTD	Accelerator	Aldrich–Sigma, Inc.		
MBTS	Accelerator	Pflatz and Baver, Inc.		
ZnO	Activator	Fisher Scientific		
Steric Acid (SA)	Activator	Fisher Scientific		

TABLE I Materials Used in This Study

by reducing the particle size and increasing the interfacial adhesion between the phases.¹³ The particle size reduction and the interfacial strengthening occur simultaneously and are coupled in conventional TPVs. An individual effect by either the particle size or the interfacial adhesion alone on the mechanical properties is difficult to deconvolute in these TPVs. Blends of thermoplastics and reclaimed rubber particles, whose size cannot be reduced as a result of interfacial modification, offer us an opportunity to decouple these factors and observe solely the effect of interfacial adhesion by the addition of an interfacial modifier.

A polypropylene (PP) resin was employed in this study for blending with ground tire rubber crumbs to prepare a TPV. To increase the adhesion between the PP matrix and reclaimed rubber particles of the TPV, PP-derived macromolecules were synthesized as interfacial modifiers. The PP molecular chains could be degraded in a controlled manner to produce terminal double bonds in the molecules,^{15,16} which were subsequently reacted via hydrosilylation with a hydride-terminated polydimethylsiloxane (PDMS) to generate hydrosilylated polypropylene (DP-HS).^{17,18} This hydrosilylation reaction was extended to join the degraded polypropylene (DEPP) and rubber molecules together and produce a graft copolymer. Three types of modified PPs with reactive functional groups were tailor-made as interfacial agents, and their effects on the mechanical and rheological properties of PP/recycled rubber crumb blends are presented.

EXPERIMENTAL

Materials

The materials and designations used in this study are shown in Table I. The rubber crumbs were evaluated according to ASTM E 11-95 standards for sieves used in industry.¹⁹ All materials were used as received.

Reactive mixing

The modified PPs were prepared with the following steps: the degradation of PP, subsequent hydrosilylation, and the mixing of DP–HS with styrene–butadiene rubber (SBR). A batch mixer (Haake Rheocord 90, Karlsruhe, Germany) with Banbury rotors was used for all the mixing, and the torque curves were recorded to monitor the reaction progress. The control temperature was 180°C, and the rotors were run at 30 rpm.

Degradation of PP

The PP resin was melted in the batch mixer and degraded with certain amounts of an organic peroxide (Luperox 101, Atofina Canada Inc.) to generate double bonds in the molecules through well-known scission reactions.¹⁶ The degradation of the PP melt was marked by a sudden drop in the torque during mixing (cf. Fig. 1), which leveled off 12 min after the addition of the peroxide. Different peroxide concentrations were used to control the DEPP chain lengths in the derived copolymers, and the torque values during reactive melt mixing were recorded. The per-oxide concentration levels and the average plateau torque values are listed in Table II.

Hydrosilylation of DEPP

The DEPP melt was immediately hydrosilylated by the addition of the desired amount of hydride-terminated PDMS along with the platinum (Pt) catalyst

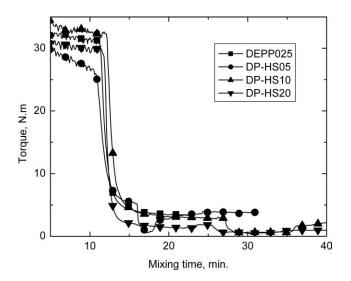


Figure 1 Torque variations during the degradation and hydrosilylation of PP.

and the cocatalyst (PDMS/Pt catalyst/cocatalyst weight ratio = 10 : 1 : 1) and by another 20 min of mixing. The PDMS was in excess to the double bonds generated in DEPP to produce live DP-HS: PP capped with PDMS. The torque values were monitored for the reaction progress.

Synthesis of the copolymer of DP-HS grafted onto SBR (PP-HS-SB)

The live DP–HS was reacted further with the double bonds present in the rubber. SBR was added to the DP–HS melt in the mixer in certain proportions. The mixing was continued for 30 min as the torque curves reached a plateau; the values were averaged and are shown in Table II. The DP–HS–SB block copolymer or graft samples were obtained at the end of the mixing.

TPV preparation

These copolymers (10 parts by weight) were blended with PP (40 parts) and 80-mesh rubber crumbs (RC80; 50 parts). Curing agents, if any, were added after the torque reached an equilibrium level, and the blending time for the dynamic vulcanization was 20 min.

Specimen preparation

The compounds from the Haake mixer were hotpressed at 180–190°C into 2-mm-thick plaques. Dumbbell tensile specimens were punched out from the plaques with an ASTM 421 cutting die.

Mechanical property measurements

Tensile tests were conducted on a tensile tester (model 4465, series IX, system 8.12.00, Automated Materials Testing, Instron, Norwood, MA) according to ASTM D 412 98a at an overhead speed of 10 mm/min. The clamp distance was 56 mm, and the gauge length was 40 mm. Measurements from six specimens were averaged for each sample.

Interfacial characterization

Each blend sample was precracked and fractured at room temperature. The fractured surface was coated with a layer of gold approximately 120 Å thick and

 TABLE II

 Recipe and Torque Values for the Degradation and Hydrosilylation of PP and the Grafting Between PP and SBR

		Degradation		
Designation	PP (parts by weight)	Peroxide (wt %)	TQ _a (N m)	TQ _b (N m)
DEPP025	100	0.25	31	6
DEPP025	100	0.25	29	7
DEPP050	100	0.5	32	3
DEPP100	100	1.5	30	1.5
		Hydrosilylation		
	DEPP (parts by weight)	PDMS (wt %)	Pt/cocatalyst (mL)	TQ _c (N m)
DP-HS05	DEPP025/100	5	1/1	4.5
DP-HS10	DEPP050/100	10	1/1	2.5
DP-HS20	DEPP100/100	20	1/1	1.0
		Grafting		
	DP-HS (parts by weight)	SBR (parts by weight)	TQ _d (N m)	
DP-HS05-SB	DP-HS05/50	50	11.5	
DP-HS10-SB	DP-HS10/50	50	7.0	
DP-HS20-SB DP-HS20/50		50	3.0	

	Recipe							Properties			
Polymers (parts by weight)			Curing agents (phr)			Tensile					
PP	Interfacial agents	RC80	S	MBTS	TMTD	SA	ZnO	strength (MPa)	Elongation at break (%)	Modulus (MPa)	Energy at break (MJ/m ³)
100											
40		60						9.6 ± 0.6	26 ± 4	25 ± 3	2.1 ± 0.5
40	DP-HS05-SB/10	50						10.4 ± 0.5	45 ± 4	31 ± 2	4.3 ± 0.2
40	DP-HS10-SB/10	50						11.0 ± 0.3	33 ± 4	33 ± 1	3.2 ± 0.5
40	DP-HS20-SB/10	50						9.2 ± 0.3	37 ± 7	27 ± 1	3.1 ± 0.7
40	DP-HS10/10	50						12.7 ± 0.4	24 ± 5	33 ± 5	2.5 ± 0.5
40	DP-HS05-SB/10	50	1	0.25	0.5	0.5	2.5	10.0 ± 0.5	37 ± 9	27 ± 2	3.4 ± 0.7
40	DP-HS10-SB/10	50	1	0.25	0.5	0.5	2.5	10.0 ± 0.8	22 ± 3	31 ± 2	1.9 ± 0.4
40	DP-HS10-SB/10	50	3	0.75	1.5	1	5	9.6 ± 0.7	14 ± 2	37 ± 3	1.1 ± 0.3
40	DEPP025/10	50	1	0.25	0.5	0.5	2.5	11.1 ± 0.6	15 ± 2	25 ± 1	1.3 ± 0.2

TABLE III Tensile Properties of the PP/RC80 Blends

was observed under a scanning electron microscope (Leo 1530, Carl Zeiss, Goetingen, Germany). Energydispersive X-ray spectroscopy (EDX) was conducted for the rubber particles and the PP matrix, and the EDX spectrum was acquired after an accumulation time of 2 min.

Rheological measurements

Pellets of PP blends were melted and extruded through five capillary dies [diameter = 0.03"; length/diameter (L/D) = 1, 5, 10, 20, or 40; entrance angle = 90°] at nine shear rates (5, 10, 20, 40, 100, 200, 400, 1000, and 2000 s⁻¹) on a capillary rheometer (Kayeness Galaxy V, Morgentown, PA), and the steady-state forces required to extrude the melts through the dies were recorded. Bagley correction was performed to obtain the entrance pressure (P_{ent}) drop data, which were used for the shear stress correction. The P_{ent} drop data were used to evaluate the effect of interfacial modification on the rheological behavior of the blends.

RESULTS AND DISCUSSION

Interfacial strengthening agents

To create strong interfacial adhesion in PP/RC80 blends, PP-derived interfacial agents were fabricated by melt-reactive mixing to introduce chemical bonding between the PP matrix and the rubber particles. The interfacial modifiers were compatible with PP because of their PP segments. On the other hand, they had functional groups that could react with the double bonds in the rubber particles. Three types of interfacial modifiers were derived from PP by peroxide degradation and hydrosilylation techniques,^{16–18} as described in the previous sections: DEPP containing terminal double bonds, live DP–HS with terminal silicon hydride bonds,

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and DP–HS–SB grafts. The incorporated functional groups—double bonds and silicon hydride in PDMS—thus could react with the rubber particles via covulcanization or hydrosilylation and provide chemical coupling between the phases. The PP–SBR grafts could offer physical adhesion to the SBR particles without vulcanization.

Melt synthesis of the interfacial agents

Figure 1 shows the torque variations for the melt mixing of the PP resin and other reactant ingredients. An abrupt drop in the torque curve occurred immediately after the addition of the organic peroxide. The torque decreased as a result of the reduction of the PP molecular weight and leveled off in approximately 10 min. Hydrosilylation of DEPP was then conducted by the addition of hydride-terminated PDMS along with the Pt catalyst and cocatalyst. There was a decrease in the torque after the addition of the hydrosilylation chemicals, but the torque increased as the liquid chemicals were consumed readily by the reaction with PP molecules (cf. Fig. 1). Several DEPP, DP-HS, and DP-HS-SB samples were prepared with the formulations shown in Table II. The plateau values of the torque curves in each stage during the reactive mixing are also recorded in Table II. TQ_a and TQ_b are the plateau torque values before and after the addition of organic peroxide, respectively, and TQ_c and TQ_d are the torque levels at the end of hydrosilylation and grafting, respectively. The monitoring of the torque variations during the reactive mixing allowed us to estimate the progress of the reaction and control the reaction conversion. We believe that the plateau regions on the torque curves indicate the completion of a reaction.

Generally, lower torque values imply a shorter molecular chain in the melt if the structures are similar.

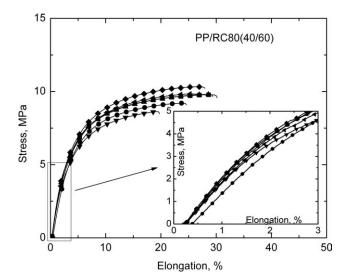


Figure 2 Tensile curves of the PP/RC80 (40/60) blend.

We expected the torque levels after the addition of peroxide (TQ_b) to decrease with an increase in the amount of peroxide. TQ_c and TQ_d values changed in the same way. Different PP-derived interfacial agents are shown in Table II and were used for PP/RC80 blends.

Tensile properties of the TPVs

Table III shows the mechanical properties of PP/RC80 blends with and without the interfacial agents. For the unvulcanized blends with DP-HS-SB grafts, PP and SBR in the grafts offered good compatibility with the PP phase and RC particles, respectively. An increase in the elongation at break and energy at break of their blends was observed in comparison with the PP/RC80 (40/60) blend. The tensile strength also increased in these blends, except for the PP/DP-HS20-SB/RC80 blend. The reason was the short chain length of DEPP in the graft, which was caused by the higher concentration of peroxide in the degradation. For the modifier without SBR (DP-HS10), the terminal silicon hydride in PDMS appeared to react with the double bonds in the SBR particles, and this led to the enhanced tensile strength of its blend.

In the vulcanized blends, covulcanization between SBR in the grafts or DEPP and the double bonds in the rubber particles forced the interfacial modifiers to the interface and bridged the two phases. The graft, DP–HS05–SB, showed its ability to improve the elongation at break and energy at break in comparison with the uncompatibilized blend. However, vulcanization decreased the elongation at break.

The various interfacial strengthening agents improved the mechanical properties of the blends to different extents by varying the degree of interfacial adhesion, which depended on the chain length and functional groups. Also, we observed that the

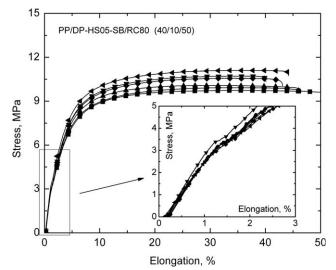


Figure 3 Tensile curves of the PP/DP–HS05–SB/RC80 (40/10/50) blend.

improvements were fairly pronounced because they did not change the shapes and sizes of the rubber crumbs in the blends, as discussed later.

Tensile curves of the TPVs

The stress–strain curves of unvulcanized PP/RC80 (40/60) blends are shown in Figure 2. Six specimens for the same sample are presented to give an estimation of the data scattering. After the initial increase, the stress leveled off, and the elongation at break was around 20–30%. In the case of the PP/DP–HS05–SB/RC80 (40/10/50) blend, as shown in Figure 3, the curves exhibit similar overall trends, but the elongation at break almost doubled. The blend was unvulcanized, and thus there was no chemical

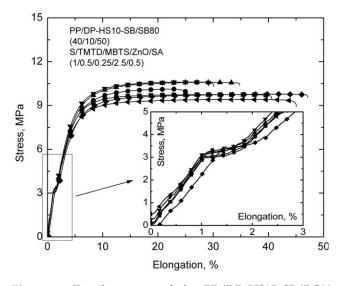


Figure 4 Tensile curves of the PP/DP–HS05–SB/RC80 (40/10/50) blend vulcanized by S/MBTS/TMTD/ZnO/SA (1/0.25/0.5/2.5/0.5).

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coupling between the interfacial modifier and rubber particles. It appears that the physical adhesion between the SBR segment of the DP–HS–SB graft and the rubber particles was good enough to allow the blend to be stretched to 50% before it broke. Tensile curves for the blend when it was vulcanized by a sulfur (S) system are shown in Figure 4.

All the curves have a kink in the region of approximately 3% elongation and approximately 4-MPa stress, as shown more clearly in the inset of Figure 4. For clearer observation, an enlargement of the region of the kink is also shown in Figure 4. For the unvulcanized blend, as shown in the inset of Figure 3, there is a distinct change in the slope for each of the tensile curves. This was not the case for the blend without the interfacial strengthening agent, as shown in Figure 2.

Similarly to the systems with interfacial agents, the PP/DEPP025/RC80 (40/10/50) blend, vulcanized with S/tetramethylthiuram disulfide (TMTD)/ 2-benzothiozolyl disulfide (MBTS)/zinc oxide (ZnO)/steric acid (SA; 1/0/5/0.25/2.5/0.5), showed the same distinctive kink on its tensile curves (inset of Fig. 5). The PP/DP–HS10/RC80 (40/10/50) blend showed similar kinks in its tensile curves (cf. Fig. 6). These kinks were located in the region of 1–2% strain and 3–4-MPa stress on their stress–strain curves, and they appeared to be related to the interfacial strengthening behavior in this system.

Such a kink, indicating a yield, on the stress–strain curves at this location has not been reported in the literature so far. The mechanism for this phenomenon needs to be further investigated. The kinks are very similar in shape to the plastic flows or so-called cold flows of the semicrystalline homopolymers polyethylene and PP after the yield/overshoot on

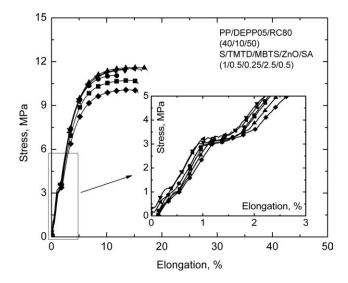


Figure 5 Tensile curves of the PP/DEPP025/RC80 (40/10/50) blend vulcanized by S/MBTS/TMTD/ZnO/SA (1/0.25/0.5/2.5/0.5).

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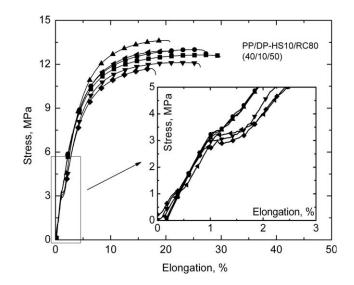


Figure 6 Tensile curves of the PP/DP-HS10/RC80 (40/10/50) blend.

their tensile curves, which originate from the orientation and alignments of the mobile interconnecting molecules between the amorphous phase and crystallites or microcrystals.²⁰ Because of the irregular shapes of the rubber crumb particles in the blends, the kinks found in our tensile curves, though much smaller, may be similarly attributed to the interfacial layers formed on the rubber particles by the interfacial modifiers, which resided at the interface of the blends, as shown in the next section by scanning electron microscopy (SEM) and EDX analysis.

Fractographs and interfacial chemical compositions

Figure 7 shows SEM micrographs of PP/RC80 (40/60) and PP/DP-HS05-SB/RC80 blends. The irregular rubber particles can be clearly seen in the fractographs for both blends, and the particle size appears to be the same. Although the rubber particle size was 80 mesh, which corresponded to 180 µm, we did not observe any particle size greater than 100 µm. The primary rubber crumbs, as received, may have been aggregates of several finer particles, and the particles themselves or the particle aggregates could be broken into finer dispersions during the intensive melt mixing (a high torque value). Two spots in each blend were chosen to be the rubber particles and the PP matrices [marked A and B in Fig. 7(a) and D and C in Fig. 7(b)]. EDX spectra were acquired for these spots and are shown in Figure 8(a-d). For the blend with no interfacial agent, the EDX spectra of the two spots appear to show just carbon and gold from the coating [cf. Fig. 8(a,b)] from either PP or RC particles/carbon black. However, the peak intensities of silicone and oxygen were substantial on the EDX spectra of the two spots in the blend with the PP-HS-SB graft. Because the

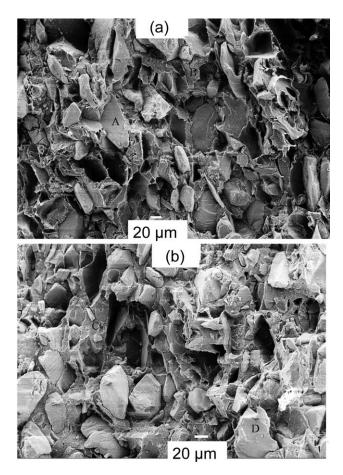


Figure 7 SEM photomicrographs of (a) the PP/RC80 (40/60) blend and (b) the PP/DP–HS05–SB/RC80 (40/10/50) blend.

PP–HS–SB graft molecules were composed of PDMS, which connected the PP and SBR portions together by chemical bonds, we could confidently attribute the silicon and oxygen peaks to PDMS of the PP–SBR graft. The concentrations of silicon and oxygen on the rubber particles [Fig. 8(d)] were much higher than those on the PP matrix, and this indicated that there was a layer of the PP–SBR graft on the rubber particles.

Rheological measurements

The viscosities of PP and its blends were measured on a capillary rheometer, and the Bagley correction was completed with a set of dies with different L/Dvalues. Figure 9 shows a typical Bagley correction plot for the PP/DP–HS10/RC80 blend. The force on the piston for each die increased as the L/D value became larger. An increase in the shear rate also led to increasing force on the piston. The entrance force was obtained by extrapolation of the lines to an L/Dvalue of 0. The corrected force to calculate the corrected stress was the total force at each shear rate with the entrance force subtracted. Figure 10 shows

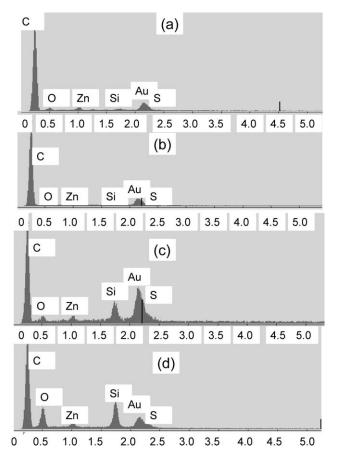


Figure 8 EDX spectra of four spots marked in Figure 7: (a) A, (b) B, (c) C, and (d) D.

the uncorrected and corrected viscosities as functions of the shear rate. Before the correction, the data from different dies varied significantly, but all the data from different dies for the same blend fell into a narrow range around a single line after the Bagley correction was applied.

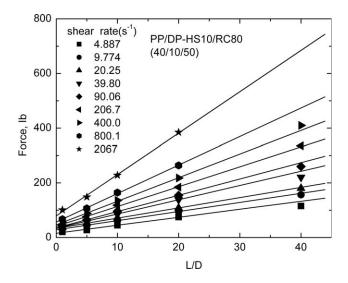


Figure 9 Bagley correction plot of the plunger force versus L/D for the PP/DP-HS10/RC80 (40/10/50) blend.

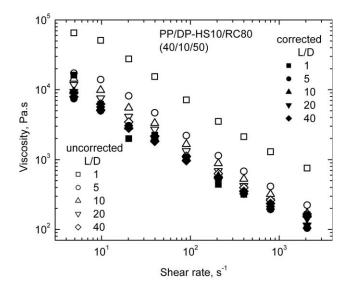


Figure 10 Corrected and uncorrected shear viscosity versus the shear rate for the PP/DP–HS10/RC80 (40/10/50) blend.

Figure 11 shows the corrected viscosity for PP and its blends as a function of the shear rate after the Bagley correction from the die with L/D = 10 was applied. Although the range of changes in the viscosity was small, we observed that the viscosity of the PP/RC80 blend was the highest at all shear rates, whereas the PP/DP–HS05/RC sample had the lowest shear viscosity level. The PP resin and all other blends had intermediate shear viscosities. To obtain more reliable data, the data from four dies (L/D = 5, 10, 20, or 40) were averaged for each sample and are shown with confidence bars in Figure 12. The trend was the same as that for the data from the single die in Figure 11. The envelope formed by the viscosity of the PP melts and binary

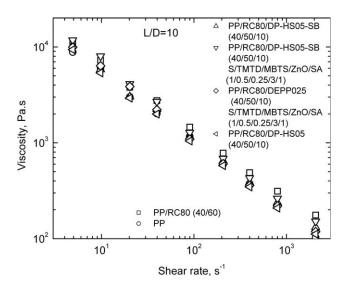


Figure 11 Corrected shear viscosity versus the shear rate for PP and its blends in the die (L/D = 10).

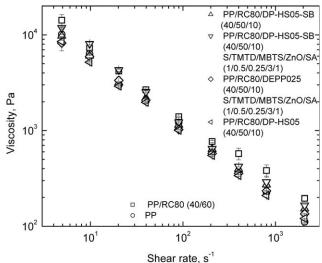


Figure 12 Corrected shear viscosity versus the shear rate averaged from four dies (L/D = 5, 10, 20, or 40) for PP and its blends.

PP/RC80 (40/60) blend encompassed all the viscosities of all the other ternary blends. The interfacial modifiers reduced the shear viscosity in comparison with the binary blend.

Because the entrance force or pressure drop is a result of shear and elongation deformation,²¹ all dies used in this study had an entrance angle of 90°; the entrance vortex was absent in this case (it existed only outside a cone angle of 120°, as experimentally verified for PP melts²¹). The ratio of elongational and shear deformation was defined by the entrance angle of the dies. The entrance force was converted into P_{ent} for all the samples, and this is plotted as a function of the shear stress in Figure 13. The PP/RC80 sample had lower P_{ent} values than all the

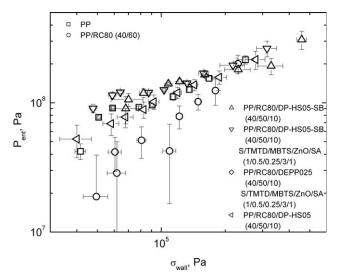


Figure 13 P_{ent} drop from Bagley correction as a function of the shear stress at die wall for PP and its blends.

other blends. The vulcanized PP/RC80/DP-HS05-SB blend had the highest level of P_{ent} . This trend was more significant at lower shear stresses, and the difference tended to be indistinguishable at higher wall shear stresses. Because P_{ent} values were proportional to the elongational viscosity, which was sensitive to the interfacial properties, a higher P_{ent} value appeared to suggest stronger interfacial adhesion.²² Thus, we can conclude that the interfacial strengthening agents increased the elongational viscosity. This observation is consistent with the literature.²² However, the interfacial strengthening led also, in sharp contrast, to the reduction in the shear viscosity, as shown in Figures 11 and 12.

CONCLUSIONS

Effects of interfacial strengthening in PP/rubber crumb blends on the ultimate mechanical properties were noticeable when the particle size was not changed by the PP-derived interfacial agents. The PP chain length and the functional groups in the interfacial agents affected the magnitude of the enhancement.

The grafting of PP molecules onto rubber molecules was achieved via stepwise hydrosilylation of hydride-terminated PDMS with the double bonds in PP and rubber molecules. The reactions were conducted during melt mixing, and torque curves were used to monitor the reaction progress.

There was a layer of interfacial modifiers formed on the rubber particles in the blend, as verified by the EDX analysis of the fractographs of the blends. This interfacial layer on the rubber particles led to a conspicuous kink in the tensile curves during an early stage of elongation (1–2% strain and 3–3.5-MPa stress). This phenomenon has not been reported before and is related to the flow of mobile molecules in the interfacial layers on the rubber particles in the blends. This interfacial layer in the blends reduced the shear viscosity and increased the P_{ent} drop and thus the elongational viscosity of the blends.

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